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Original Research

Biogas Production from Maize Grains and Maize Silage

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Abstract

The main objective of this work was anaerobic digestion of maize grains and maize silage and biogas production from these crops. Maize grains were treated using one-stage and two-stage anaerobic techniques; using hydrolysis and acidification as the first stage and methanogenesis as the second stage. Processing nonacidified maize grains in an anaerobic reactor is more stable, though the anaerobic degradation start-up period is longer, specific production of biogas is lower and excess sludge production is higher as from acidified maize grains. Maximum specific biogas production was 0.72 $m^3 \cdot kg^{-1}$ of volatile suspended solids – VSS (nonacidified maize) (at 35ºC) and 0.770 $m^3 \cdot kg^{-1}$ VSS (acidified maize) during anaerobic digestion of maize grains. At average yield of 9 $t \cdot ha^{-1}$ of dry maize 5,450 $Nm^3 \cdot ha^{-1}$ of methane can be generated from nonacidified maize and 5,828 $Nm^3 \cdot ha^{-1}$ methane from acidified maize grains.

Due to low nitrogen content in maize silage, anaerobic digestion of maize silage is rather unstable. Alkali or complementary substrates with higher nitrogen content (e.g. excess sludge from wastewater treatment plant or manure) can be used for anaerobic process stabilization. Maximum measured biogas specific production from maize silage reached 0.655 $m^3 \cdot kg^{-1}$ VSS. At average yield of 30 $t \cdot ha^{-1}$ of the dry maize silage 9,058 $Nm^3 \cdot ha^{-1}$ of methane can be generated.

Keywords: anaerobic digestion, biogas production, maize grains, maize silage

Introduction

Energy crops are one alternative for how to diversify agricultural production and enhance the business of a farm. Biogas energy can be used to improve the energy balance of a farm itself, or the excess energy can be offered for sale (e.g. to an electricity network). Maize, which in a form of silage offers interesting yields (about 30 tons of total solids - TS per hectare [1-3]), was selected as an energetic crop in this paper. The possibility of maize grain treatment was also studied. It is obvious that maize grains, both from economic and nutritional points of view, are not the most suitable material for biogas production, since a large portion of production costs was used to obtain dry and pure grains. Despite this, attention has been paid to this material, as well. Experience shows that there are periods in an agricultural commodities market when maize grains cannot be sold or are sold deeply below its production costs. Then, maize grains that are too inefficient to be sold, can be used as a supplementary material for biogas production.

In general, there is only little information on maize grain anaerobic digestion available in literature. Pouech et al. [4],

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deal with anaerobic digestion of maize grains. In a batch laboratory reactor under mesophilic conditions, specific production of methane of 0.397 m^3 kg^{-1} of the dry maize grains was achieved.

Similarly, there is only a very little information on anaerobic digestion of maize silage as an only substrate. Generally, it may be said that studies focusing on anaerobic digestion of fresh or ensiled materials did not show significant differences in biogas production, which is discussed, e.g. in Zubr [5]. Conservation qualities are an advantage when using silage, i.e. it may be used year round regardless to the season. Negligible differences in biogas production from fresh or silage material also are presented in the work of Gunaseelan [6].

Anaerobic digestion of maize silage is mentioned by Zauner and Küntzel [5]. In batch laboratory reactors, they achieved specific methane production of 0.270 – 0.289 $m^3 \cdot kg^{-1}$ of the TS. In a laboratory flow reactor, specific methane production was a little bit lower – 0.181-0.184 $m^3 \cdot kg^{-1}$ of the TS.

Amon et al. [2], dealt with biogas production from energetic crops – maize and clover grass, in more detail. In their work, the team focused on biogas production from various varieties of maize in various stages of ripeness (milk ripeness, wax ripeness and full ripeness). Different varieties reached the harvesting optimum in different stages of ripeness. Specific methane production ranged from 0.206-0.286 $Nm^3 \cdot kg^{-1}$ VSS and methane yield ranged from 5,300 to 8,530 $Nm^3 \cdot ha^{-1}$. These results were achieved in mesophilic (40ºC) batch tests of anaerobic degradation, which lasted for 60 days. Some varieties showed minimal difference in the methane production, depending on the stage of harvest. Some varieties showed a difference of more than 25% (Saxxo variety, vax ripeness, Amon et al. [2]).

Specific methane yields of 0.282-0.419 $Nm^3 \cdot kg^{-1}$ VSS was obtained in the study of Schittenhelm [8], which dealt with the effect of maize composition and its stage of maturity on the methane yields. These results are comparable with other information in the literature [3, 9-12]. In the work [8], specific methane yields of the late maturity hybrids largely increased with sampling date, whereas the climatically adapted medium-early hybrids reach their maximum methane production at an earlier date. The same tendency was observed by Schumacher et al. [12] in a harvest date experiment with a broad maturity spectrum of maize hybrids.

In our work, we focused on determining conditions for anaerobic digestion of maize grains and maize silage, long-term operation of maize grains and maize silage anaerobic digestion laboratory models and on obtaining technological parameters of the process.

Experimental

In the experimental part of our work, laboratory tests of maize grain (hereinafter referred to as the "maize") and maize silage anaerobic degradation were carried out and maize hydrolysis and acidification tests were carried out, as well. Long-term operation of laboratory models for anaerobic treatment of nonacidified and acidified maize and maize silage was also monitored.

Prior to its processing, maize grains were milled to the size of approximately 2 mm. The size of particles in silage was not adjusted in the lab tests, i.e. it was of a size to which it was adjusted by the harvesting machine. Most of the silage particle sizes were ranging several cm. Average TS of the maize used was 90.6%, volatile suspended solids (VSS) of TS 92.8%. Average TS of silage was 35%, VSS 95.8%. Value of pH of maize water leachate (mixture of 100 g maize topped up to 400 ml with tap water) was 5.9; pH of water leachate of the silage (in the same ratio with water) was 2.7.

At the beginning, batch tests of anaerobic degradation were carried out. The same anaerobically stabilized sludge was used for these tests as for the laboratory models inoculation. Total volume of the mixture during the tests was 1 l, therefore the volume of used anaerobically stabilized sludge was 0.5 l, 3 g of maize or 6 g of silage (dry matter), topped up to 1 l with tap water. Blank tests to measure biogas production by the anaerobic sludge itself were also carried out.

The maize was treated in a one- and two-stage anaerobic semi-continuous laboratory model. The two-stage model consisted of hydrolysis and acidification in the first stage and methanization in the second stage. To first stage, the maize was dosed in a mixture of 25 g of maize filled to 100 ml with tap water. Retention time of the mixture in this stage was 4 d. This retention time was selected as a result of the hydrolysis and acidification test. Their results are presented below. Acidification mixture volume increased with methanogenic reactor loading rate growth.

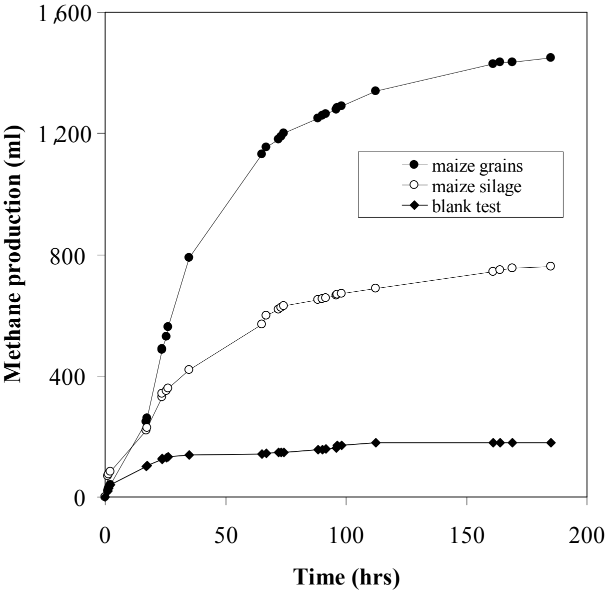

Fig. 1. Tests of anaerobic degradation of maize grains and maize silage (amount of dry maize grains at test – 3 g, amount of dry silage at test – 6 g, amount of anaerobically stabilised sludge at all tests – 0.5 l, with concetration of TS 37.23 $g \cdot l^{-1}$ and VSS 20.74 $g \cdot l^{-1}$).

Table 1. Acidification test of the maize grains.

Day	pH	$COD_{fil.}$ [$mg\cdot l^{-1}$]	$COD_{unfil.}$ [$mg\cdot l^{-1}$]	VFA [$mg\cdot l^{-1}$]
0	5.9	5,860	18,830	332
1	3.8	10,100	20,470	2,040
2	3.7	14,350	31,380	2,500
3	3.7	16,440	36,300	3,620
4	3.6	23,200	38,500	8,520
6	3.5	28,700	42,000	10,500
7	3.3	33,480	46,010	11,400

fil. – filtered sample;
unfil. – unfiltered sample.

Mixed methanogenic reactor volume was 4 l. In the one-stage system, the maize was treated without acidification. Silage was processed without prior acidification and was fed into the methanogenic reactor directly, having the same quality as that delivered from silage pits. All methanogenic reactors (both for treatment of maize and silage) were filled by anaerobically stabilized sludge from the Wastewater Treatment Plant Bratislava-Vrakuňa to half of their volume; sludge concentration of 37.2 $g\cdot l^{-1}$ TS and VSS of 55.7%, and were topped up with tap water to 4 L. Laboratory models were fed once a day and worked as chemostates. All experiments were carried out at temperature of 35ºC. Concentrations of chemical oxygen demand (COD), volatile fatty acids (VFA), ammonia nitrogen and pH value were monitored in filtered samples of sludge water from methanogenic reactors. In the reactors, concentrations of suspended solids and production of biogas were monitored. Standard methods [13] were used to carry out all analysis. Analysis of VFA was made according to Kapp [14]. GA 2000 Plus (Geotechnical Instruments, UK) apparatus was used to measure the content of biogas (methane, CO_2, H_2 and H_2S).

Results and Discussion

Tests of Anaerobic Degradation, Hydrolysis and Acidification

Fig. 1 shows the results of anaerobic degradation tests; about 470 ml of methane were obtained from one gram of the TS (maize) and about 233 ml of methane from one gram of dry silage. These quantities are in compliance with data stated by Amon et al. [2].

Then the maize acidification test was carried out (Table 1). COD of filtered and unfiltered sample, VFA and pH, were monitored in the mixture of maize and water (100 g of maize topped up to 400 ml with tap water). An acidification test was carried out since the maize contains a significant amount of polysaccharides and proteins, and their hydrolysis and acidification separate from the methanogenic phase can accelerate anaerobic degradation. Acidification test results show that a sufficient acidification period is 4 days.

The technology of maize silage production when it is stored in silage pits for several weeks or months shows that acidification will not be necessary in this case and it is possible to feed it directly into a methanogenic reactor.

Laboratory Models Operation

Anaerobic Digestion of Nonacidified Maize

A gradual increase of organic loading rate (OLR) in the methanogenic reactor is obvious from Table 2. In the period of nonacidified maize treatment, the initial OLR of the methanogenic reactor was 1.05 $kg\cdot m^{-3}\cdot d^{-1}$ (VSS), the maximum achieved OLR was 6.3 $kg\cdot m^{-3}\cdot d^{-1}$. According to Table 2, specific biogas production ranged from 0.420 m^3 to 0.720 m^3 per kilogram of the VSS (maize). Maximum achieved specific biogas production per unit volume of the reactor was 4.5 $m^3\cdot m^{-3}\cdot d^{-1}$ for a day. Maximum specific biogas production was 0.720 m^3 per kilogram of VSS at OLR 5.25 $kg\cdot m^{-3}\cdot d^{-1}$. Fig. 2 shows a cumulative biogas production from nonacidified maize during the methanogenic reactor operation.

Table 2. Operational parameters of the methanogenic reactors during the anaerobic digestion of nonacidified and acidified maize grains.

Dose of maize (raw material)	Dose of maize (VSS)	Organic loading rate (VSS)	Nonacidified maize		Acidified maize	
			Day of operation	Specific biogas production (VSS)	Day of operation	Specific biogas production (VSS)
[$g\cdot d^{-1}$]	[$g\cdot d^{-1}$]	[$kg\cdot m^{-3}\cdot d^{-1}$]		[$m^3\cdot kg^{-1}$]		[$m^3\cdot kg^{-1}$]
5	4.2	1.05	0-10	0.420	0-10	0.510
10	8.41	2.1	11-50	0.510	11-20	0.590
12.5	10.51	2.63	51-80	0.595	21-50	0.630
20	16.82	4.2	81-210	0.660	51-100	0.715
25	21.03	5.25	211-260	0.720	101-200	0.770
30	25.23	6.3	261-300	0.710	201-300	0.680

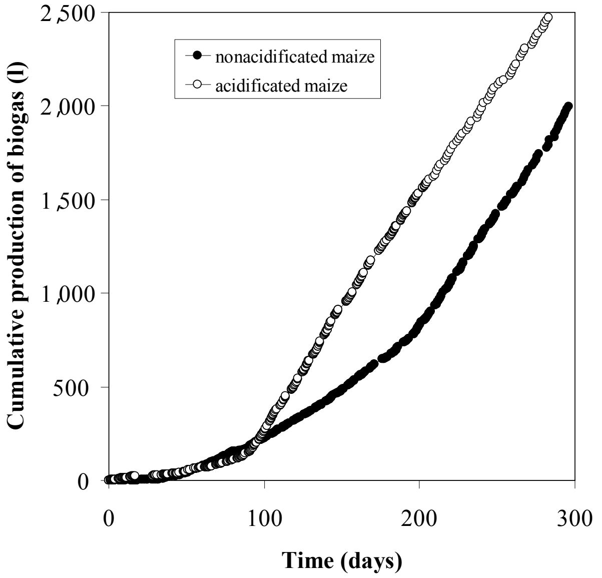

Fig. 2. Cumulative production of biogas from nonacidified and acidified maize grains.

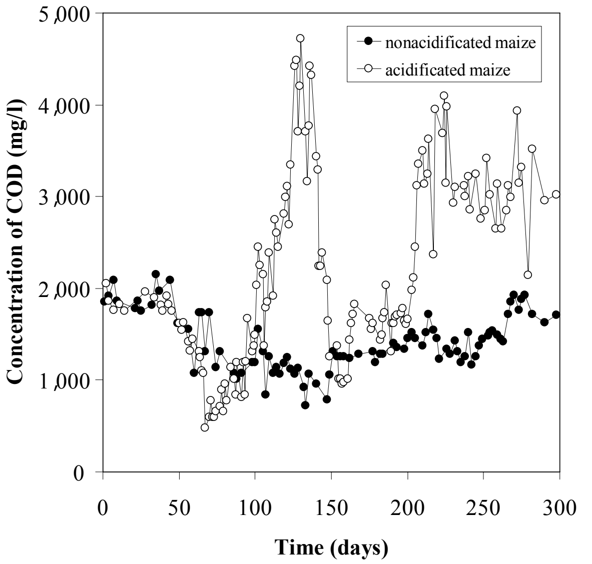

Fig. 3. Concentration of COD in sludge water in the methanogenic reactor during the treatment of nonacidified and acidified maize grains (filtered sample).

Figs. 3-5 show the course of monitored parameters in the sludge water from the methanogenic reactor. Operation of methanogenic reactor was stable during the whole period of anaerobic digestion of nonacidified maize. COD concentration is shown in Fig. 3; VFA concentration in Fig. 4 and ammonia nitrogen concentration is shown in Fig. 5. pH values were very stable and varied in the range 7-7.2. Measured average concentrations of monitored parameters in the period of maximum specific biogas production (between day 211 and 260): COD 1406 mg·l^{-1}, VFA 612 mg·l^{-1} and ammonia nitrogen 610 mg·l^{-1}. After increasing organic load to 6.3 kg·m^{-3}·d^{-1}, COD and VFA (Figs. 3 and 4), concentrations increased and specific biogas production decreased. Therefore, we consider organic load of 5 kg·m^{-3}·d^{-1} as the optimal value.

Concentration of suspended solids in the methanogenic reactor gradually increased, being 41.5 g·l^{-1} at the end of the operation. Specific excess sludge production was calculated on the basis of the suspended solids balance; its value was 0.15 g·g^{-1} of maize TS.

Average composition of biogas produced from nonacidified maize is shown in Table 3.

Anaerobic Digestion of Acidified Maize

As already mentioned, retention time of the maize and water mixture in the acidification stage was 4 days. Dosage of acidified maize in individual periods of methanogenic

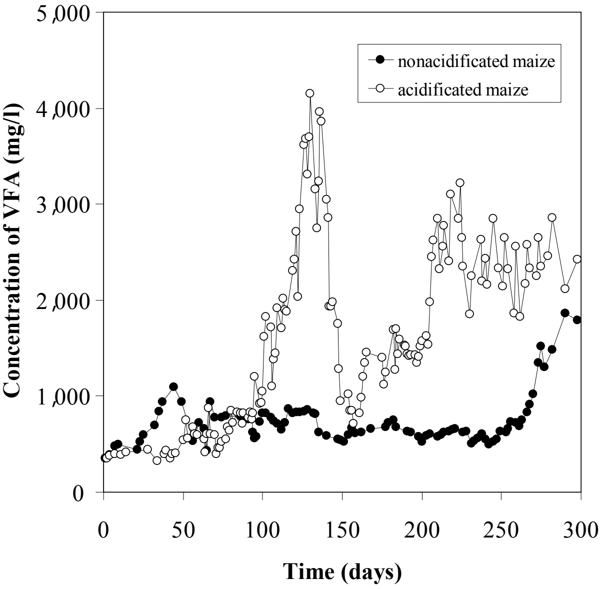

Fig. 4. Concentration of VFA in sludge water in the methanogenic reactor during the treatment of nonacidified and acidified maize grains (filtered sample).

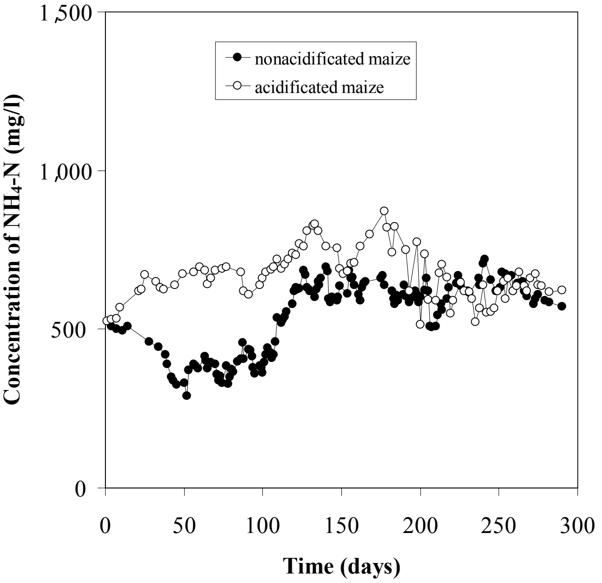

Fig. 5. Concentration of NH_4-N in sludge water in the methanogenic reactor during the treatment of nonacidified and acidified maize grains (filtered sample).

Table 3. Composition of biogas produced from maize grains and maize silage.

Component	Biogas from nonacidified maize	Biogas from acidified maize	Biogas from silage
CH_4 [%]	54.8	55.5	54.5
CO_2 [%]	44.9	44.3	45.4
H_2 [ppm]	10	90	215
H_2S [ppm]	170	170	5

Table 4. Operational parameters of the methanogenic reactor during the anaerobic digestion of maize silage.

Day of operation	Dose of silage (raw material)	Dose of silage (VSS)	Organic loading rate (VSS)	Specific biogas production (VSS)
	[$g \cdot d^{-1}$]	[$g \cdot d^{-1}$]	[$kg \cdot m^{-3} \cdot d^{-1}$]	[$m^3 \cdot kg^{-1}$]
0-20	20	6.71	1.68	0.195
21-40	30	10.06	2.52	0.230
41-80	40	13.42	3.36	0.430
81-120	50	16.77	4.19	0.530
121-220	60	20.12	5.03	0.655
220-300	80	26.83	6.71	0.420

reactor operation is shown in Table 2. Since the start of the methanogenic reactor operation, biogas production was higher than for the nonacidified maize. Therefore, it was possible to increase organic load faster. According to Table 2, the specific biogas production was ranging from 0.510 m^3 to 0.770 m^3 per kilogram of the VSS (maize). Maximum achieved specific biogas production per unit volume of the reactor was 4.3 $m^3 \cdot m^{-3} \cdot d^{-1}$ for a day. Maximum specific production of biogas was 0.770 m^3 per kilogram of VSS at OLR 5.25 $kg \cdot m^{-3} \cdot d^{-1}$. Fig. 2 shows a cumulative production of biogas from acidified maize during the methanogenic reactor operation. The comparison of cumulative biogas production from nonacidified and acidified maize showed that a high rate of biogas production was reached faster (after 100 days of operation) from acidified maize than from nonacidified maize (after more than 200 days of operation). It is obvious from Figs. 3 and 4 that the operation of the methanogenic reactor treating acidified maize was not as stable as in the case of nonacidified maize. After increasing organic loading rate to 5.25 $kg \cdot m^{-3} \cdot d^{-1}$, COD and VFA concentrations increased significantly and gradually stabilized at levels below 2,000 $mg \cdot l^{-1}$ (COD) and 1,700 $mg \cdot l^{-1}$ (VFA). ORL increase to 6.3 $kg \cdot m^{-3} \cdot d^{-1}$ caused a permanent increase of COD and VFA concentrations and the specific biogas production was also reduced. Optimal OLR for anaerobic digestion of acidified maize was 5.25 $kg \cdot m^{-3} \cdot d^{-1}$. Values of pH were in the range 6.5-7.8.

Ammonia nitrogen concentrations (Fig. 5) show a very interesting development. Nitrogen from acidified and hydrolyzed maize was immediately released to the sludge water. After approximately 130 days, ammonia nitrogen concentration in the sludge water from nonacidified maize treatment reached the values of acidified maize.

Suspended solids concentration in the methanogenic reactor gradually increased and reached 35.6 $g \cdot l^{-1}$ at the end of the operation. Specific excess sludge production was calculated on the basis of the suspended solids balance; its value was 0.13 $g \cdot g^{-1}$ of maize TS.

Composition of biogas from acidified maize is shown in Table 3.

Comparison of anaerobic digestion of nonacidified and acidified maize showed that:

- anaerobic digestion of nonacidified maize was more stable;
- methanogenic reactor start-up period was significantly shorter in the case of acidified maize;
- specific biogas production was higher by 7% in the case of acidified maize;
- specific excess sludge production was lower by 15% in the case of acidified maize;
- biogas from acidified maize had a slightly higher content of methane.

After anaerobic biomass adaptation, the rate of maize acidification and hydrolysis were sufficient in the methanogenic reactor. It is obvious that if the maize is used in a biogas plant as a supplementary material alongside other substrates, it is not necessary to acidify it before it is fed into the methanogenic reactor.

Anaerobic Digestion of the Maize Silage

The silage treated in the anaerobic reactor had the same quality as when delivered from silage pits. Reactor operation parameters are shown in Table 4.

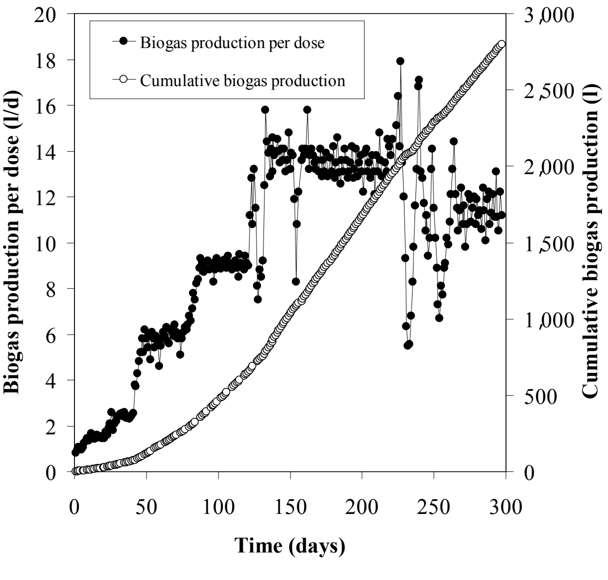

Fig. 6. Production of biogas per dose of maize silage and cumulative production of biogas in the methanogenic reactor.

Table 5. Achieved parameters of the anaerobic digestion of maize grains and maize silage.

Parameter	Dimension	Maize		Silage
		nonacidified	acidified	
ORL (VSS)	kg·m^{-3}·d^{-1}	5.25	5.25	5.03
Suspended solids in reactor	g·l^{-1}	41.5	35.6	79
Specific biogas production (35ºC)	m^3·kg^{-1}	0.720	0.770	0.655
Specific methane production	Nm^3·kg^{-1}	0,35	0.380	0.316
Specific excess sludge production	g·g^{-1}	0.15	0.13	0.17
Degradation of TS	%	85	87	83.0

Fig. 6 shows biogas production per dose of the maize silage, and cumulative biogas production during gradual load of the methanogenic reactor. Organic loading rate in the reactor increased from 1.68 to 6.71 kg·m^{-3}·d^{-1} (Table 4). Specific biogas production varied from 0.195 to 0.655 kg per kg of silage VSS. Maximum specific production of biogas was reached at OLR 5.03 kg·m^{-3}·d^{-1}. It is obvious from Figs. 6-8 that the methanogenic reactor operation was not as stable as in the case of grain maize treatment. COD and VFA concentrations were rising rapidly after each increase of OLR (Fig. 7). Stabilized COD and VFA values lasted several days or weeks, after a dose increase. Duration of stabilization period depended on the depth of destabilization after a dose increase. At higher doses of silage, response on OLR increase was stronger and the stabilization period was longer. In these periods, pH values dropped below 6.5 – Fig. 8. Sodium bicarbonate was used to adjust pH values. pH was not stable even after COD and VFA concentrations stabilized; therefore, pH was adjusted during the whole operation of methanogenic reactor. The reactor was fed with 100 g of $NaHCO_3$ during 300 days of its operation, which corresponds to a sodium bicarbonate dose of about 0.33 g.d^{-1} into a 4 L reactor, or 0.08 kg per m^3 of reactor per day.

In comparison with the course of the pH values in the reactor for the treatment of acidified and nonacidified maize, the pH values during treatment of silage have been more unstable. This stability in the case of maize treatment can be explained by a higher concentration of ammonia ions in the sludge water, as maize is richer in proteins than silage (Fig. 5 vs. Fig. 8). Alongside a carbonate buffer system ($CO_2/CO_3^{2-}/HCO_2^-$), ammonium buffer system (NH_3/NH_4^+) also plays an important role in anaerobic processes. The study shows that when maize silage is the sole substrate processed in a biogas plant, doses of alkali or complementary substrates with higher nitrogen content (e.g. excess sludge from wastewater treatment plant or manure) need to be added.

At the OLR of 6.71 kg·m^{-3}·d^{-1}, COD and VFA concentrations exceeded 18,000 mg·l^{-1} and 11,000 mg·l^{-1}, respectively (Fig. 7). It is obvious that the anaerobic reactor was

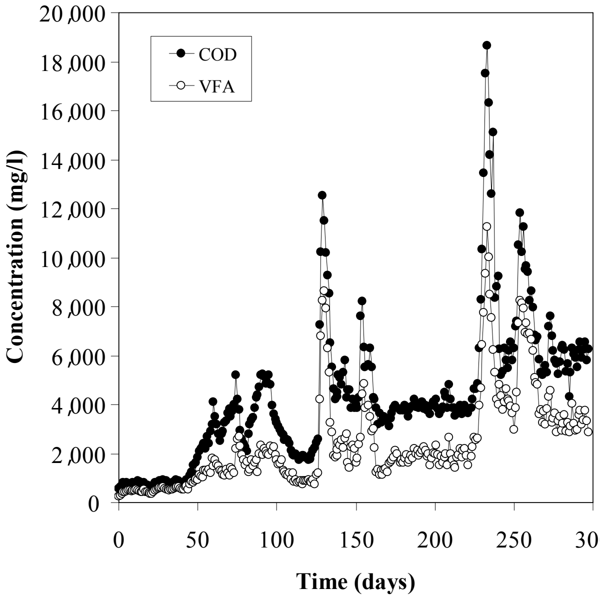

Fig. 7. Concentrations of COD and VFA in the sludge water in the methanogenic reactor during the treatment of maize silage (filtered sample).

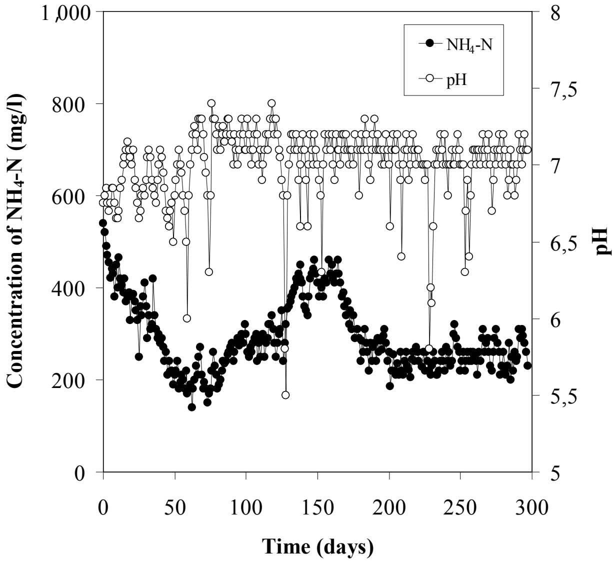

Fig. 8. Concentrations of NH_4-N and pH values in the sludge water in the methanogenic reactor during the treatment of maize silage (filtered sample).

overloaded when silage dose increased. High VFA concentrations caused a significant methanization inhibition, which resulted in a temporary reduction in biogas production. COD and VFA concentrations were stabilized at around 6,000 mg·l^{-1} and 2,800 mg·l^{-1}, respectively. At this OLR, the specific biogas production amounted 0.420 kg·kg^{-1} of VSS, which is significantly less that with OLR values of 5.03 kg·m^{-3}·d^{-1} (0.655 kg·kg^{-1} of VSS). Therefore, 5.03 kg·m^{-3}·d^{-1} is considered to be the optimum OLR value.

Average concentration of suspended solids in the anaerobic reactor was 79 g·l^{-1} during the stable period of operation (between days 121-220). The daily amount of excess sludge was 3.57 g. For a dose of 21 g TS (60 g of raw silage, dry matter 35%), this represents the excess sludge production of 0.17 g per gram of silage TS. Therefore, the degree of anaerobic degradation of silage material was 83.0%.

Content of individual components of biogas from maize silage is shown in Table 3.

Table 5 summarizes the results from anaerobic digestion of nonacidified maize, acidified maize and maize silage.

Assuming that 1 ha of arable land produces 9 t of grain maize (TS), then 5,450 Nm^3·ha^{-1} methane can be obtained from nonacidified maize, or 5,828 Nm^3·ha^{-1} methane from acidified maize. If 30 t of maize silage (TS) is obtained from 1 ha, then the production of methane is 9,058 Nm^3·ha^{-1}. For a biogas plant with electrical output of 1 MW burning biogas in a cogeneration unit, maize from about 1.1 ha or maize silage from 0.67 ha is needed for its daily operation; taking 90% efficiency of cogeneration unit and the 1:1.5 ratio of produced electrical and thermal energy as a base for calculations.

Conclusions

Anaerobic digestion of maize in laboratory conditions shows that the operation of an anaerobic reactor is more stable when nonacidified maize is processed, though the start-up period of anaerobic degradation is longer, specific production of biogas is lower and production of excess sludge is higher compared to acidified maize. It would depend on the decision of a biogas plant designer whether the 7% higher production of biogas and consequent electricity production will cover the investments and operational costs of a more complex technology needed for the acidification of maize.

Anaerobic digestion of maize silage produced interesting yields of biogas per unit of processed material. However, due to the low nitrogen content in maize silage the operation of an anaerobic reactor is rather unstable. Alkali or complementary substrates with higher nitrogen content (e.g. excess sludge from wastewater treatment plant or manure) can be used for the stabilization of anaerobic processes.

For a biogas plant with electrical output of 1 MW burning biogas in a cogeneration unit, maize from about 1.1 ha or maize silage from 0.67 ha is needed for its daily operation.

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